

REMARKS

Claims 1-13, as amended, remain herein. Claims 1, 2, 8 and 9 have been amended. Support for the amendments may be found throughout the specification (see, e.g., page 11, lines 9-18; page 50, line 17 to page 21, line 8 of the specification).

1. Claims 1-13 were rejected under 35 U.S.C. § 112, first paragraph. Claim 1 has been amended to moot this rejection. A person of ordinary skill in the art can, without undue experimentation, measure the Energy Gap and Ionization Potential by using the methods recited in claim 1, which are widely used in this art.

2. Claim 9 was rejected under 35 U.S.C. § 112, second paragraph. Claim 9 has been amended to moot this rejection.

3. Claims 1-5 were rejected under 35 U.S.C. § 102(e) over Hatwar et al. U.S. Patent 6,967,062 with evidence of inherency supplied by Lim et al. (*Journal of Organometallic Chemistry* 2006, 691, 2701-2707) or Hatwar U.S. Patent 7,037,601.

Applicants' claim 1 recites an organic electroluminescence device emitting white light which comprises a pair of electrodes, at least two light emitting layers and an electron transporting layer comprising a heterocyclic derivative having a (at least one) nitrogen atom, the light emitting layers and the electron transporting layer being between the pair of electrodes, wherein an energy gap of a host compound comprised in each light emitting layer Eg(Host-i) satisfies following relation (I):

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$$2.9 \text{ eV} \leq E_g(\text{Host-}i) \quad \cdots (\text{I})$$

wherein  $E_g(\text{Host-}i)$  represents an energy gap of a host compound comprised in an  $i$ -th light emitting layer from the electron transporting layer,  $i$  representing an integer of 1 to  $n$ ,

an energy gap of the heterocyclic derivative having a nitrogen atom comprised in the electron transporting layer  $E_g(\text{ETM})$  satisfies following relation (II):

$$2.9 \text{ eV} < E_g(\text{ETM}) \quad \cdots (\text{II})$$

and an ionization potential of a host compound comprised in a light emitting layer adjacent to the electron transporting layer ( $I_p(\text{Host-}1)$ ) and an ionization potential of the heterocyclic derivative having a nitrogen atom comprised in the electron transporting layer ( $I_p(\text{ETM})$ ) satisfy following relation (III):

$$I_p(\text{ETM}) \leq I_p(\text{Host-}1) + 0.3 \text{ eV} \quad \cdots (\text{III})$$

Hatwar does not disclose applicants' claimed an organic electroluminescence device. Hatwar says nothing about the Ionization Potential and Energy Gap relationships of the host compound and the heterocyclic derivative having a nitrogen atom of the electron transporting layer. Hatwar discloses multiple possible materials for the electron transporting layer. Hatwar, however, does not recognize or disclose applicants' superior organic electroluminescence device including an electron transporting material having an energy gap greater than 2.9 eV. All of Hatwar's examples use Alq not BAQ as the electron transporting layer. In fact, BAQ is used in Hatwar's light emitting layer, but not in Hatwar's electron transporting layer. As shown in the enclosed Mori et al. article, the energy gap of Alq is 2.6 eV which is below the claimed 2.9 eV.

Applicants' claimed organic electroluminescence device recites a novel and non-obvious combination of Ionization Potential and Energy Gap relationships of the host compound and the

heterocyclic derivative having a nitrogen atom of the electron transporting layer. None of Hatwar's exemplified devices discloses applicants' claimed Ionization Potential and Energy Gap relationship combination.

Thus, Hatwar does not disclose all elements of applicants' claims and therefore, it is not an adequate basis for a rejection under 35 U.S.C. § 102(e).

Applicants' claims are also non-obvious over Hatwar. Evidence rebutting an obviousness rejection includes evidence that the claimed invention yields unexpectedly improved properties or properties not present in the prior art. In re Dillon, 919 F.2d 688, 692-93 (Fed. Cir. 1990); MPEP § 2145. Applicants' claimed organic electroluminescence device provides a great efficiency of light emission under a low voltage and has a long lifetime, and exhibits no change in the chromaticity (see Abstract and Table 1 in applicants' specification (comparing Examples 1-6 to Comparative Examples 1-3)).

Thus, applicants' claimed organic electroluminescence device is neither anticipated nor obvious. Applicants respectfully request reconsideration and withdrawal of this rejection.

4. Claims 6-7 were rejected under 35 U.S.C. § 103(a) over Hatwar et al. U.S. Patent 6,967,062 with evidence of inherency allegedly supplied by Lim et al. in view of Nakamura et al. U.S. Patent 6,509,109.

As discussed above, Hatwar does not teach or suggest all elements of applicants' claim 1. Nakamura does not teach or suggest what is missing from Hatwar.

Thus, none of Hatwar and Nakamura discloses or suggests applicants' claimed invention. In addition, there is no disclosure or suggestion in any of Hatwar, Nakamura, or anything else in

this record that would have suggested the desirability of combining any portions thereof effectively to anticipate or render obvious applicants' claimed invention. Applicants respectfully request reconsideration and withdrawal of this rejection.

5. Claims 8-13 were rejected under 35 U.S.C. § 103(a) over Hatwar et al. U.S. Patent 6,967,062 with evidence of alleged inherency supplied by Lim et al. in view of Kim et al. PCT Patent Publication 02/088274.

As discussed above, Hatwar does not teach or suggest all elements of applicants' claim 1. Kim does not teach or suggest what is missing from Hatwar. Kim says nothing about applicants' claimed combination of Ionization Potential and Energy Gap relationships of the host compound and the heterocyclic derivative having a nitrogen atom of the electron transporting layer.

Evidence rebutting an obviousness rejection includes evidence that the claimed invention yields unexpectedly improved properties or properties not present in the prior art. In re Dillon, 919 F.2d 688, 692-93 (Fed. Cir. 1990); MPEP § 2145. Applicants' claimed organic electroluminescence device provides a great efficiency of light emission under a low voltage and has a long lifetime, and exhibits no change in the chromaticity (see Abstract and Table 1 in applicants' specification (comparing Examples 1-6 to Comparative Examples 1-3)).

Furthermore, Hatwar teaches organic compounds as electron transporting materials (see Hatwar at column 7, lines 30-31) but states that metal chelated oxinoid compounds are preferred materials for use in forming the electron transporting layer. Thus, a person of ordinary skill in the art would not be motivated to use Kim's organic non-metallic compound.

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Thus, none of Hatwar and Kim discloses or suggests applicants' claimed invention. In addition, there is no disclosure or suggestion in any of Hatwar, Kim, or anything else in this record that would have suggested the desirability of combining any portions thereof effectively to anticipate or render obvious applicants' claimed invention. Applicants respectfully request reconsideration and withdrawal of this rejection.

Accordingly, this application is now fully in condition for allowance and a notice to that effect is respectfully requested. The PTO is hereby authorized to charge/credit any fee deficiencies or overpayments to Deposit Account No. 19-4293. If further amendments would place this application in even better condition for issue, the Examiner is invited to call applicants' undersigned attorney at the number listed below.

Respectfully submitted,

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## Lost Hole-Blocking Property of Blue-Emitting Alq by Inserting Detached Layer

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The authors found an interesting and strange phenomenon that is inexplicable using a simple energy diagram. Blue-emitting Alq (BAIq), a hole-blocking material, exhibits an excellent hole-blocking property in an organic light-emitting diode (LED) consisting of naphthalyl-substituted diamine derivative (NPD) and BAlq. Nevertheless, its hole-blocking property is lost by inserting Alq<sub>3</sub> between BAlq and a cathode. This fact suggests that an indirect interaction is imparted to the NPD/BAlq interface from a detached (not neighboring) layer. In addition, difference electroluminescence (EL) spectrum analysis is very effective in the discussion of EL mechanism. [DOI: 10.1143/JJAP.44.6772]

KEYWORDS: organic light-emitting diode, difference EL spectrum, blue-emitting Alq, hole-blocking property

### 1. Introduction

Organic light-emitting diodes (OLEDs), as reported by Tang and coworkers,<sup>1,2</sup> are a notable as a component of flat-panel displays. They use aluminum quinoline (Alq<sub>3</sub>). This metal complex is popular and excellent as an emitting material, a host emitting material, and an electron-transport material. OLEDs, particularly those with low molecular weight, consist of many organic layers. In addition, each organic layer plays an important role according to its separate function. For example, copper phthalocyanine (CuPc)<sup>3</sup> and starburst materials<sup>4</sup> are well known as hole-injection materials, triphenylamine derivatives as a hole-transport materials, 4,7-diphenyl-1,10-phenanthroline (BCP)<sup>5</sup> and aluminum(III) bis(2-methyl-8-quinolinolate)4-phenylphenoxyate (BAlq)<sup>6–10</sup> as hole-blocking materials, and oxadiazole derivatives<sup>11</sup> as electron-transport materials.

Recently, BAlq has often been used as a hole-blocking material and as a host material for phosphorescent dyes. However, VanSlyke *et al.* initially reported it as a blue emitting material and as a host material for another blue emitting dye in 1996.<sup>12</sup> The authors fabricated OLEDs with a BAlq emission material and reported their electroluminescence (EL) properties.<sup>13</sup> They also demonstrated the following: EL spectra in NPD/BAlq OLEDs changed with increasing applied current. The introduction of an electron-transport layer, Alq<sub>3</sub>, improved the EL efficiency. In addition, because it influenced EL spectra, the recombination zone was suggested to differ from those of OLEDs without an Alq<sub>3</sub> layer. The authors speculated on the cause of the above phenomena.

In this paper, the authors report that the EL mechanism and recombination zone can be elucidated easily in detail by difference EL spectrum analysis.

### 2. Experimental

The authors used copper phthalocyanine (CuPc) as a hole-injection layer, *N,N'*-di(1-naphthyl)-*N,N'*-diphenyl-1,1'-diphenyl-1,4'-diamine (NPD) as a hole-transport layer, and 8-hydroxyquinoline aluminum (Alq<sub>3</sub>) and BAlq as an emitting materials. Sublimated CuPc, NPD, and Alq<sub>3</sub> were obtained from Nippon Steel Chemical Co., Ltd. An NPD thin film was prepared on a glass substrate with an indium-tin-oxide (ITO) transparent electrode (anode). Organic thin films were prepared by vacuum deposition at *ca.* 0.81 ×

10<sup>−3</sup> Pa at room temperature. Typical deposition rates of organic materials were about 0.2–0.3 nm/s. For the upper metal electrode (cathode), the effective electrode area of the specimens was 2 × 2 mm<sup>2</sup>.

Absorption spectra were measured using a spectrophotometer (U-3000; Hitachi). Photoluminescence (PL) spectra were also measured with a spectrophotometer (FP-777; JASCO). The ionization potentials of the organic films and the work functions of the ITO and metal were estimated using an atmosphere ultraviolet photoelectron analysis device (AC-2; Riken Keiki).

Efficiency-current-voltage characteristics were measured using a source measure unit (238 High Current Source Measure unit; Keithley Instruments) and a luminance meter (BM-8; TOPCON). Luminance-current-voltage characteristics were measured under vacuum: *ca.* 0.1 Pa. EL spectra were obtained using photonic multichannel analyzer-10 (PMA-10; Hamamatsu Photonics). The operating time dependences of these spectra were obtained using a high-sensitivity spectro-multichannel photo detector (MCPD-4500; Otsuka Electronics). The external quantum efficiency of OLED,  $\eta_{ext}$ , was calculated on the basis of the front luminance and EL spectra under the assumption of a uniformly diffusive surface,

$$\eta_{ext} = \frac{\pi e L_0}{K_m h c J} \frac{\int i_{el}(\lambda) \lambda d\lambda}{\int i_{el}(\lambda) \cdot V(\lambda) d\lambda},$$

where *e* represents the elementary charge, *L<sub>0</sub>*, the front luminance, *K<sub>m</sub>*, a constant of 683 lm/W, *h*, Planck's constant, *c*, light velocity, *J*, the current density, *i<sub>el</sub>(λ)*, the relative EL intensity at the wavelength *λ*, and *V(λ)*, the spectral luminosity efficiency at *λ*.

### 3. Experimental Results and Discussion

Figure 1 shows the current density dependence of EL spectra for ITO/CuPc (20 nm)/NPD (50 nm)/BAlq (50 nm)/LiF (0.6 nm)/Al as shown in a previous paper.<sup>13</sup> The EL shoulder at 450 nm increases with applied current. The main recombination zone is located near the interface between the hole-transport layer and the emission layer when the OLED comprises a hole-transport layer and an emission layer. Therefore, the increasing EL component is attributable to the hole-transport material, NPD. In fact, the difference EL

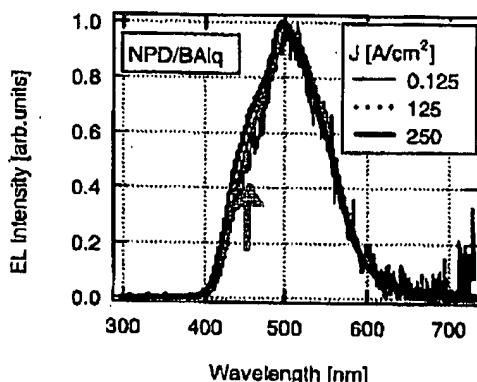


Fig. 1. Current density dependence of EL spectra in ITO/CuPc (30 nm)/NPD (50 nm)/BAIq (50 nm)/LiF (0.6 nm)/Al.

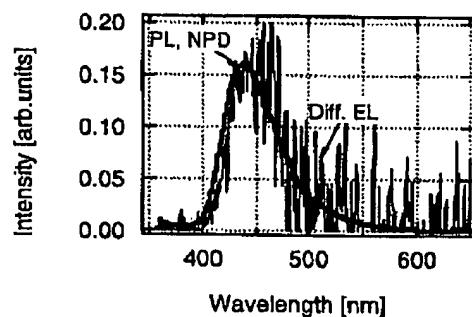


Fig. 2. Difference EL spectrum (increasing EL) between high- and low-current regions with PL due to NPD.

spectrum of EL at 250 mA/cm<sup>2</sup> minus EL at 0.125 mA/cm<sup>2</sup> is shown with the PL spectrum of NPD in Fig. 2. The difference EL component is assigned as the EL due to NPD.

This difference component suggests that the recombination zone is enlarged between the BAIq and NPD layers with increasing current, as shown in Fig. 3.

When the EL spectrum has several EL components, each EL component is assignable by the peak-separation method. However, it is not easy to define the standard EL spectrum of a material for OLEDs because the EL, from the effect of an organic dye, is modified by the interference of the metal cathode and surrounding conditions of the emitting molecule. Consequently, the EL spectrum changes with a shifting, broadening and narrowing deformation. However, disregarding quantitative percentage, it can be easily judged whether an EL component is included in an EL spectrum by difference EL spectrum analysis between two normalized EL spectra. Of course, the disadvantage of the difference EL spectra method is that such strange EL spectra partially lack a negative EL component, which appears between energetically neighboring EL spectra. Generally, because all EL components from the organic dyes used are known, it is possible to discuss qualitative phenomena.

Figure 4 shows the current density dependence of EL spectra in ITO/NPD/BAIq/Alq<sub>3</sub>/LiF/Al, as shown in a previous study.<sup>13)</sup> The introduction of an Alq<sub>3</sub> layer between BAIq and LiF enhanced the external quantum efficiency of OLEDs and suppressed the EL shoulder at around 450 nm. Figure 5 shows the difference EL spectrum between the EL of OLED with NPD (50 nm)/BAIq (50 nm) and the EL of OLED with the NPD (50 nm)/BAIq (10 or 25 nm)/Alq<sub>3</sub> (40 or 25 nm); it agrees with the NPD PL. That is, the insertion of Alq<sub>3</sub> is suggested to induce the shift of the recombination zone from both the NPD and BAIq layers to the BAIq and Alq<sub>3</sub> layers. If the Alq<sub>3</sub> layer enhances electron injection and electron transport into BAIq, more electrons should be transported to the interface between NPD and BAIq. Consequently, more electrons penetrate the NPD layer. Thereby, the use of an Alq<sub>3</sub> electron transport layer should enhance recombination on NPD. Nevertheless, the above

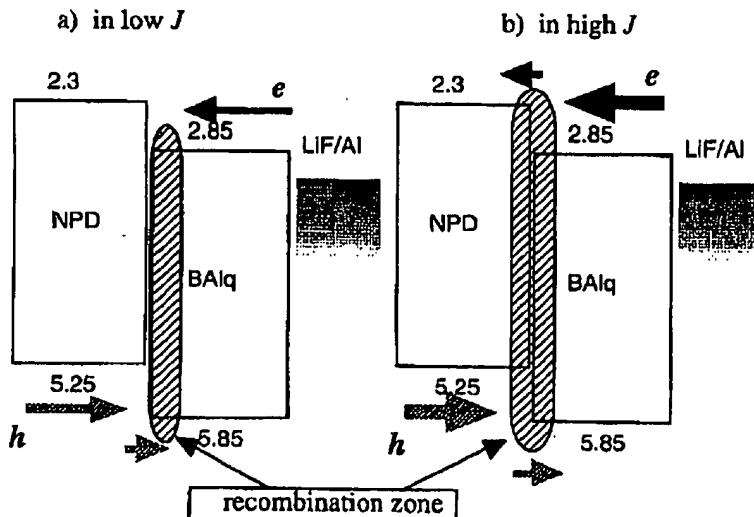


Fig. 3. Energy diagram of NPD/BAIq/LiF/Al: (a) low-current-density region and (b) high-current-density region. Arrows show electron or hole flows. The shaded area shows the recombination zone.

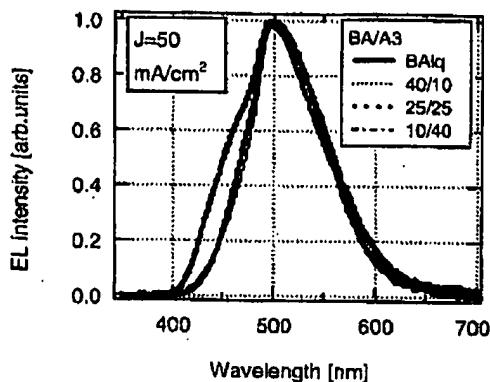


Fig. 4. EL spectra for NPD/BAIq, NPD/BAIq ( $x$  nm)/Alq3 (50 -  $x$  nm) at 50 mA/cm<sup>2</sup>.

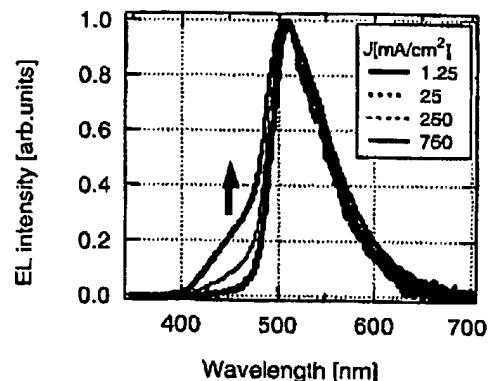


Fig. 6. Current density dependence of EL spectra in ITO/CuPc (30 nm)/NPD (50 nm)/BAIq (30 nm)/C540-doped Alq3 (10 nm)/Alq3 (10 nm)/LiF (0.6 nm)/Al.

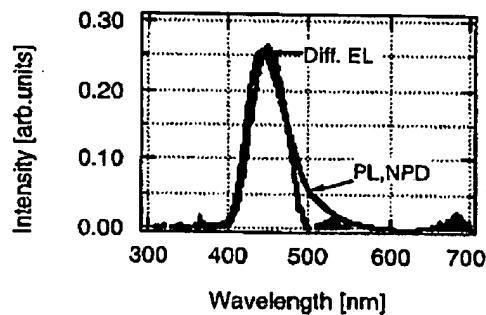


Fig. 5. Difference EL spectrum (decreasing EL) between BAIq and BAIq (10 nm)/Alq3 (40 nm) with PL due to NPD.

speculation is not consistent with our experimental results. For this reason, we attempted to determine the location of the recombination zone using a partial dye-doping method.

Figure 6 shows the current density dependence of EL spectra for ITO/CuPc (20 nm)/NPD (50 nm)/BAIq (30 nm)/C540-doped Alq3 (10 nm)/Alq3 (10 nm)/LiF (0.6 nm)/Al. The EL spectrum of a partially C540-doped device almost completely agrees with that of a C540-doped Alq3 LED at  $J < 25$  mA/cm<sup>2</sup> in the previous study.<sup>(13)</sup> This result suggests that the recombination zone is located in the C540-doped Alq3 layer. In our speculation, the recombination zone in the BAIq OLEDs with a partially C540-doped Alq3 layer may be enlarged into the BAIq layer with an applied current, as shown in Fig. 7. If the EL at 450 nm is attributable to NPD, this fact implies that the recombination zone in the specimen with a C540-doped Alq3 layer is enlarged as a result of the C540-doped Alq3 layer to NPD layer including BAIq layer (30 nm). In general, however, the wide recombination zone of ca. 50 nm is judged to be unreasonable.

Figure 8 shows the difference EL spectrum of EL at 750 mA/cm<sup>2</sup> minus EL at 1.25 mA/cm<sup>2</sup> with the BAIq EL

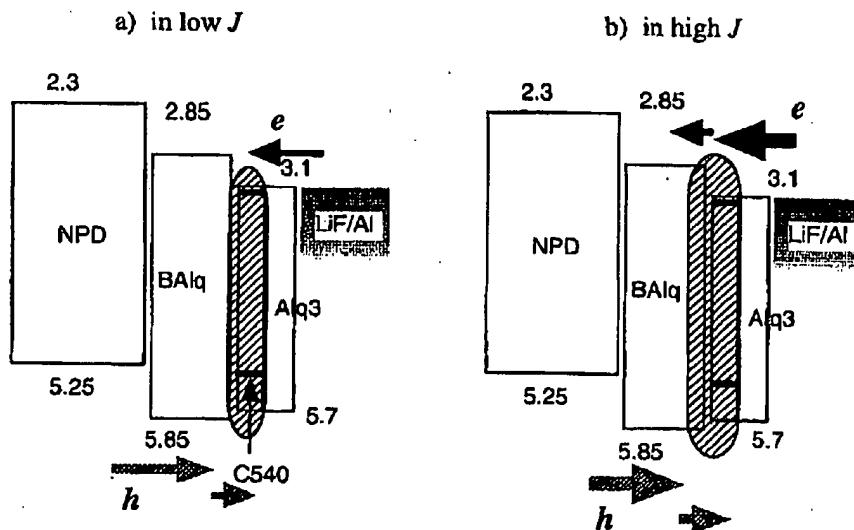


Fig. 7. Energy diagram of NPD/BAIq/C540-doped Alq3/Alq3/LiF/Al: (a) low-current-density region and (b) high-current-density region. All symbols are similar to those in Fig. 3.

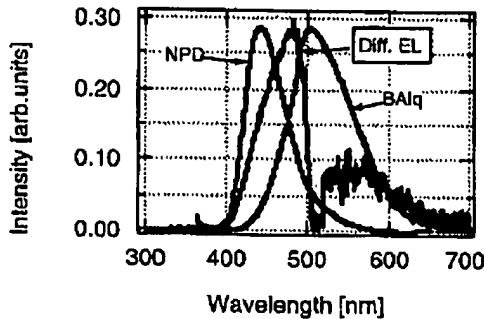


Fig. 8. Difference EL spectrum (increasing EL) between high-current and low-current regions in partially CS40-doped specimen with PL due to NPD and EL of NPD/BAIq OLED.

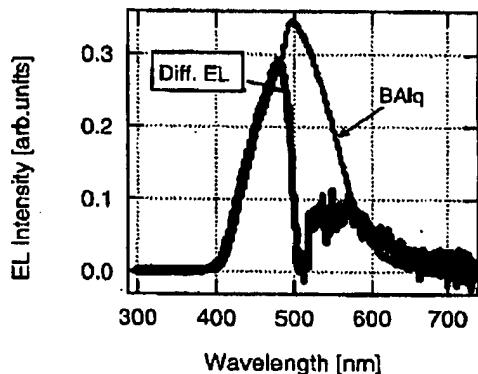


Fig. 9. Difference EL spectrum (increasing EL) with calculated EL spectrum of NPD/BAIq OLED.

and NPD PL. The difference EL spectrum is inferred to be unattributable to either BAlq or NPD and cannot be expressed as the sum of the NPD PL and BAlq EL. The authors believe that the difference EL spectrum is related to BAlq.

Figure 9 shows the difference EL spectrum and the BAlq EL spectrum. The difference EL is consistent with the high-energy shoulder of the BAlq EL spectrum. Because the EL component at around 500 nm is included in both BAlq and CS40, it disappears from the difference EL spectrum. Therefore, the recombination zone in the BAlq OLEDs with a partially CS40-doped Alq3 layer is enlarged into the BAlq layer with an applied current, as shown in Fig. 7.

Our experimental results suggest that the hole-transport property of BAlq is lost by inserting an Alq3 layer between BAlq and the cathode. In addition, once holes are injected into BAlq, they are thought to move easily in the BAlq layer. Although the hole-blocking property of BAlq is considered to be weaker than that of BCP, the barrier height of hole injection between NPD and BAlq is determined only by the energy relationship between the two materials. We always use an identical procedure to fabricate the interface between NPD and BAlq.

Holes that reach in front of the NPD/BAlq interface can

indicate the presence or absence of a 30 nm-separated Alq3 layer. In the presence of the Alq3 layer, the holes move to BAlq independent of the barrier height of the NPD/BAlq interface. On the other hand, in the absence of the Alq3 layer, the movement of the holes is inhibited by the barrier height. Considering that charged carriers are affected, it is thought that the potential around the NPD/BAlq interface is changed by inserting an Alq3 layer. However, it is highly unlikely that the barrier height of hole injection between NPD and BAlq is reduced despite the enhancement of the electric field around the NPD/BAlq interface by a separating space charge because the barrier height is probably controlled by neighboring materials. Electrons accumulating in the BAlq/Alq3 interface may act as a heterospace charge against the accumulated holes in the NPD/BAlq interface. Even so, the achievement of a strong enhanced electric field in the NPD/BAlq interface will lead to a strong reduced electric field in front of the cathode. Consequently, the electric field in front of the cathode is thought to reduce markedly until electrons cannot be injected from the cathode. Therefore, our experimental results are inexplicable using a simple energy diagram. Presently, the authors have no model to explain these experimental results, but they have studied the mechanism in detail.

#### 4. Conclusions

The authors carried out a conventional experiment to elucidate the basic conduction and EL properties of BAlq. The characteristics of the recombination zone in NPD/BAlq and NPD/BAlq/Alq3 OLEDs can be analyzed using a difference EL spectrum. The authors found that the hole-blocking property of BAlq is lost by inserting an Alq3 layer between BAlq and a cathode. This strange phenomenon is inexplicable using the simple energy diagram used by most researchers to predict OLED performance.

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